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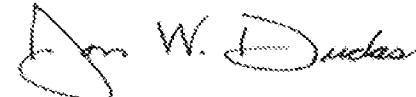
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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

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TITLE OF THE INVENTION (280 characters max)

IMPROVED PROCESS FOR CROSSLINKING FREE-RADICAL CROSSLINKABLE POLYMERS

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ENCLOSED APPLICATION PARTS (check all that apply)

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Respectfully submitted,

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PROVISIONAL APPLICATION COVER SHEET

Page 2

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TITLE OF THE INVENTION (280 characters max)

IMPROVED PROCESS FOR CROSSLINKING FREE-RADICAL CROSSLINKABLE POLYMERS

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IMPROVED PROCESS FOR CROSSLINKING FREE-RADICAL CROSSLINKABLE POLYMERS

FIELD OF THE INVENTION

This invention relates to polymer systems that undergo free radical crosslinking reactions. In particular, the invention relates to an improved process for crosslinking polymers, wherein the improved process delivers hotter processing 5 conditions, faster crosslinking, or increased crosslinked densities.

DESCRIPTION OF THE PRIOR ART

A number of polymers can undergo free radical reactions. Some of those reactions are beneficial such as crosslinking while others are detrimental such as premature crosslinking, competing, or degrading. There is a need to promote the 10 beneficial crosslinking reaction while minimizing the impact of the detrimental reactions.

Generally, as free-radical crosslinkable polymers are processed for crosslinking purposes, the polymers follow a nominal crosslinking temperature profile. The nominal crosslinking temperature profile has three temperature-related 15 portions: (1) a melt processing temperature portion; (2) a transitional temperature portion; and (3) a crosslinking temperature portion. The nominal crosslinking temperature profile is directly related to the polymer and the free-radical inducing species (or the crosslinking agent) selected. Figure 1 illustrates a typical nominal crosslinking temperature profile.

20 To ensure that only the desired crosslinking reaction occurs, the melt processing temperature is kept low to avoid premature crosslinking. After the desired level of melt processing has occurred, the crosslinkable polymer and the free-radical inducing species are subjected to a transitional temperature portion to reach the nominal crosslinking temperature. If the free-radical species is an organic peroxide, 25 the nominal crosslinking temperature is directly dependent upon the decomposition of temperature of the peroxide. Accordingly, the temperature range of the transitional temperature portion is determined by the nominal melt processing temperature on the low temperature end and by the nominal crosslinking temperature on the high temperature end.

30 Because the crosslinking rate increases gradually with temperature, the temperature difference between the melt processing temperature portion and the

crosslinking temperature portion (i.e., the transitional temperature portion) can be quite large, typically greater than about 60 degrees Celsius. While the crosslinking temperature changes with the choice of free-radical inducing species, the corresponding temperature range of the transitional temperature portion is generally 5 unaffected. Therefore, a change in the crosslinking temperature typically requires a corresponding change in the melt processing temperature.

For example, in injection molding applications, a low injection temperature (i.e., melt processing temperature portion) is required because common organic peroxides decompose over a broad temperature range. For example, practitioners 10 commonly inject crosslinkable polymer compositions containing ethylene/propylene/diene monomer-based polymers and the organic peroxide dicumyl peroxide into a mold at about 100 degrees Celsius (below the peroxide's peak decomposition temperature) and then cure the compositions in the mold with wall temperature set at about 165 degrees Celsius (i.e., crosslinking temperature portion). 15 As such, the crosslinking process has a large range for the transitional temperature about 65 degrees Celsius, which results in a very long nominal crosslinking temperature profile time, particularly for thick parts. The nominal crosslinking temperature profile restricts injection molding to those crosslinkable polymers having a suitable melting temperature or viscosity profile.

20 Similarly, practitioners extrude crosslinkable polymer compositions at temperatures no higher than 140 degrees Celsius and then pass the resulting fabricated articles through a continuous vulcanization tube at a higher crosslinking temperature, typically in excess of 200 degrees Celsius, to complete crosslinking. Because shear heating from extruder screw speed can induce premature crosslinking, the screw 25 speed is maintained at a low rate and extrusion outputs are limited.

With free-radical crosslinkable ethylene/propylene/diene monomer-based polymers or ethylene/propylene rubbers, the crosslinkable compositions are typically extruded at a temperature no higher than about 120 degrees Celsius with the extruded article ultimately passing through a continuous vulcanization tube at a temperature of 30 about 210 degrees Celsius. Similarly, free-radical crosslinkable flame retardant polyolefin-based compositions are typically extruded at a temperature no higher than about 140 degrees Celsius with the extruded article ultimately passing through a continuous vulcanization tube at a temperature of about 200 - 210 degrees Celsius.

With free-radical crosslinkable chlorinated polyethylene, the primary fabrication method is extrusion. Typically, crosslinkable polymeric compositions containing chlorinated polyethylene are melt-processed in a batch mixer and then subjected to a crosslinking conductions in a continuous vulcanization tube, usually at 5 about 200 degrees Celsius.

When these chlorinated polyethylene compositions are filled with small particle-size fillers such as carbon black and silica, intensive mixing is required. Unfortunately, the intensive mixing is limited by temperature and time to avoid premature crosslinking. In fact, the temperature is maintained at no higher than 100 10 degrees Celsius. Also, because shear heating from the extruder screw can also induce premature crosslinking, extrusion output rates are limited.

The transitional temperature for chlorinated polyethylene compositions represents about an 100-degree Celsius temperature range. This temperature difference negatively impacts the line speed and contributes to a long residence time 15 in the continuous vulcanization tube.

To increase injection temperatures or extrusion rates without premature crosslinking, practitioners add scorch inhibitors or antioxidants to the compositions. Unfortunately, this approach reduces the cure rate. To overcome the cure rate reduction, practitioners use longer continuous vulcanization tubes when extruding the 20 polymer or sophisticated formulations of the composition for injection molded or extruded polymers.

Accordingly, the need exists for an improved process for crosslinking free-radical crosslinkable polymers. The improved process must permit a higher melting temperature portion than presently achieved in conventional processes while 25 maintaining the present levels of premature crosslinking or further minimizing premature crosslinking. Similarly, the improved process must permit higher extrusion screw rates than presently practiced in conventional processes without any appreciably negative impact upon premature crosslinking.

There is also a need for an improved process for crosslinking free radical 30 crosslinkable polymers wherein the temperature range of the transitional temperature portion is significantly smaller than provided in conventional processes, also without negatively impacting premature crosslinking. A smaller temperature range will yield a faster process because the transitional heating for the polymer is minimized.

It is also desirable that the transitional temperature portion increase as sharply as possible and approach an infinite slope. Moreover, it is desirable that the crosslinking temperature portion have a slope of as near zero as possible.

5 Each of these needed process improvements should be achievable without significantly modifying the conventional crosslinking equipment. Notably, the needed improvement should not require longer continuous vulcanization tubes for extruded crosslinkable polymer articles.

10 Ultimately, there is a need for a higher melt temperature portion for free-radical crosslinkable polymers and a need for a faster crosslinking process without having a detrimental effect on the properties of the articles made by the improved process.

SUMMARY OF THE INVENTION

15 The present invention is an improved process for crosslinking polymers, wherein the improved process delivers hotter processing conditions, faster crosslinking, or increased crosslinked densities. The invented process comprises the steps of (a) melt processing a crosslinkable polymeric composition, (b) forming an article of manufacture from the crosslinkable polymeric composition, and (c) crosslinking the crosslinkable polymeric composition as a formed article of manufacture. The crosslinkable polymeric composition comprises (1) a free-radical 20 crosslinkable polymer, (2) a free-radical inducing species, and (3) a crosslinking-temperature-profile modifier.

25 The melt processing step or the crosslinking step occurs at a temperature higher than conventionally used for crosslinking polymers. The increase temperatures permit crosslinking of previously excluded polymers (due to high melting temperatures). The increased temperatures also permit rate improvements over the crosslinking profile.

BRIEF DESCRIPTION OF DRAWING

Fig. 1 shows a nominal crosslinking temperature profile for a combination of a free-radical crosslinkable polymer compositions and a free-radical inducing species.

30 Fig. 2 shows torque-time curves at 140 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

Fig. 3 shows torque-time curves at 177 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

Fig. 4 shows torque-time curves at 140 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

Fig. 5 shows torque-time curves at 182 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

5 Fig. 6 shows torque-time curves at 140 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

Fig. 7 shows torque-time curves at 182 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

10 Fig. 8 shows torque-time curves at 120 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

Fig. 9 shows torque-time curves at 140 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

Fig. 10 shows torque-time curves at 182 degrees Celsius for crosslinkable polymeric compositions with and without a crosslinking temperature-profile modifier.

15 **DESCRIPTION OF THE INVENTION**

The invented process for preparing a crosslinked article of manufacture comprises the steps of (a) melt processing a crosslinkable polymeric composition, (b) forming an article of manufacture from the crosslinkable polymeric composition, and (c) crosslinking the crosslinkable polymeric composition as a formed article of manufacture. The crosslinkable polymeric composition comprises (1) a free-radical crosslinkable polymer, (2) a free-radical inducing species, and (3) a crosslinking-temperature-profile modifier.

In the absence of the crosslinking-temperature-profile modifier, the combination of the free-radical crosslinkable polymer and the free-radical inducing species has a nominal crosslinking temperature profile. The nominal crosslinking temperature profile comprises a nominal melt processing temperature portion, a nominal transitional temperature portion, and a nominal crosslinking temperature portion.

30 The crosslinking-temperature-profile modifier permits raising the temperature of the melt processing temperature portion and reducing the transitional temperature portion. Accordingly, in the invented process, the melt processing step occurs at a temperature greater than nominal melt processing temperature of the combination.

The combination of the free-radical crosslinkable polymer and the free-radical inducing species achieves a nominal induction time ($t_{0.04n}$) at the nominal melt processing temperature. The nominal induction time is the amount of time required for the torque value as measured by a rheometer to increase by 0.04 pound-inches above the minimum torque prior to the onset of crosslinking.

At the nominal melt processing temperature, crosslinkable polymeric composition achieves an improved induction time ($t_{0.04i}$) of at least 5-fold greater than the nominal induction time. Preferably, the improved induction time is at least 10-fold greater than the nominal induction time. More preferably, the improved induction time is at least 15-fold greater.

At the elevated melt processing temperature, the crosslinkable polymeric composition achieves a cure rate equal to or faster than that which is achievable in the absence of the crosslinking temperature profile modifier over the nominal crosslinking temperature profile. Also, at the elevated melt processing temperature, the crosslinkable polymeric composition maintains an induction time equal to or greater than the nominal induction time.

Preferably, the crosslinkable polymeric composition achieves the same degree of cure or a higher degree of cure than the combination would achieve in the absence of the crosslinking-temperature-profile modifier.

The present invention is useful in wire-and-cable, footwear, film (e.g. greenhouse, shrink, and elastic), rheology modification, engineering thermoplastic, highly-filled, flame retardant, reactive compounding, thermoplastic elastomer, thermoplastic vulcanizate, automotive, vulcanized rubber replacement, construction, automotive, furniture, foam, wetting, adhesive, paintable substrate, dyeable polyolefin, moisture-cure, nanocomposite, compatibilizing, printing, steel replacement, wax, sizing, calendered sheet, medical, dispersion, coextrusion, cement/plastic reinforcement, food packaging, non-woven, paper-modification, multilayer container, sporting good, oriented structure, and surface treatment applications.

A variety of polymers is useful in the present invention. Moreover, many polymers that were heretofore unsuitable for free-radical crosslinking are useful in the present invention. Notably, polymers having a high melting temperature are now suitable for free-radical crosslinking. In particular, the present invention is useful

with free-radical crosslinking polymers having a melting temperature equal to or greater than about 130 degrees Celsius or a short nominal induction time. For example, the present invention is particularly useful for combinations of a free-radical crosslinkable polymer and a free-radical inducing species that have a nominal induction time of less than about 5 minutes or even less than about one minute.

Preferably, the free-radical crosslinkable polymer is hydrocarbon-based. Suitable hydrocarbon-based polymers include ethylene/propylene/diene monomers, ethylene/propylene rubbers, ethylene/alpha-olefin copolymers, ethylene homopolymers, propylene homopolymers, ethylene/unsaturated ester copolymers, ethylene/styrene interpolymers, halogenated polyethylenes, propylene copolymers, natural rubber, styrene/butadiene rubber, styrene/butadiene/styrene block copolymers, styrene/ethylene/butadiene/styrene copolymers, polybutadiene rubber, butyl rubber, chloroprene rubber, chlorosulfonated polyethylene rubber, ethylene/diene copolymer, and nitrile rubber, and blends thereof.

More preferably, the hydrocarbon-based polymer is selected from the group consisting of ethylene/propylene/diene monomers and ethylene/propylene rubbers. Even more preferably, when the hydrocarbon-based polymer is one of these preferable polymers or a blend thereof, the free-radical crosslinkable polymer is present in an amount between about 20 weight percent and about 88.9 weight percent, the free-radical inducing species is present in an amount between about 0.5 weight percent and 10 weight percent, and the crosslinking-temperature profile modifier is present in amount between about 0.1 weight percent and about 5 weight percent, and the free-radical crosslinkable polymeric composition further comprises inorganic fillers in an amount between about 10 weight percent and about 65 weight percent.

Also, more preferably, the hydrocarbon-based polymer is selected from the group consisting of ethylene/alpha-olefin copolymers and ethylene/unsaturated ester copolymers. Even more preferably, when the hydrocarbon-based polymer is one of these preferable polymers or a blend thereof, the free-radical crosslinkable polymer is present in an amount between about 15 weight percent and about 83.9 weight percent, the free-radical inducing species is present in an amount between about 0.5 weight percent and 10 weight percent, and the crosslinking-temperature profile modifier is present in amount between about 0.1 weight percent and about 5 weight percent, and the free-radical crosslinkable polymeric composition further comprises flame

retardant additives in an amount between about 15 weight percent and about 70 weight percent.

Also, even more preferably, when the hydrocarbon-based polymer is one of these preferable polymers or a blend thereof, the free-radical crosslinkable polymer is present in an amount between about 10 weight percent and about 82.9 weight percent, the free-radical inducing species is present in an amount between about 0.1 weight percent and 10 weight percent, and the crosslinking-temperature profile modifier is present in amount between about 2.0 weight percent and about 10 weight percent, and the free-radical crosslinkable polymeric composition further comprises flame retardant additives in an amount between about 15 weight percent and about 70 weight percent.

These even more preferred compositions are useful for flame retardant polyolefin-based compositions.

The present invention is particularly beneficial when the free-radical crosslinkable polymer is a propylene polymer because the crosslinking-temperature-profile modifier can suppress chain scission of the propylene polymer.

With regard to the suitable ethylene polymers, the free-radical crosslinkable polymers generally fall into four main classifications: (1) highly-branched; (2) heterogeneous linear; (3) homogeneously branched linear; and (4) homogeneously branched substantially linear. These polymers can be prepared with Ziegler-Natta catalysts, metallocene or vanadium-based single-site catalysts, or constrained geometry single-site catalysts.

Highly branched ethylene polymers include low density polyethylene (LDPE). Those polymers can be prepared with a free-radical initiator at high temperatures and high pressure. Alternatively, they can be prepared with a coordination catalyst at high temperatures and relatively low pressures. These polymers have a density between about 0.910 grams per cubic centimeter and about 0.940 grams per cubic centimeter as measured by ASTM D-792.

Heterogeneous linear ethylene polymers include linear low density polyethylene (LLDPE), ultra-low density polyethylene (ULDPE), very low density polyethylene (VLDPE), and high density polyethylene (HDPE). Linear low density ethylene polymers have a density between about 0.850 grams per cubic centimeter and about 0.940 grams per cubic centimeter and a melt index between about 0.01 to

about 100 grams per 10 minutes as measured by ASTM 1238, condition I. Preferably, the melt index is between about 0.1 to about 50 grams per 10 minutes. Also, preferably, the LLDPE is an interpolymer of ethylene and one or more other alpha-olefins having from 3 to 18 carbon atoms, more preferably from 3 to 8 carbon atoms.

5 Preferred comonomers include 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene.

Ultra-low density polyethylene and very low density polyethylene are known interchangeably. These polymers have a density between about 0.870 grams per cubic centimeter and about 0.910 grams per cubic centimeter. High density ethylene polymers are generally homopolymers with a density between about 0.941 grams per 10 cubic centimeter and about 0.965 grams per cubic centimeter.

10 Homogeneously branched linear ethylene polymers include homogeneous LLDPE. The uniformly branched/homogeneous polymers are those polymers in which the comonomer is randomly distributed within a given interpolymer molecule and wherein the interpolymer molecules have a similar ethylene/comonomer ratio 15 within that interpolymer.

Homogeneously-branched substantially linear ethylene polymers include (a) homopolymers of C₂-C₂₀ olefins, such as ethylene, propylene, and 4-methyl-1-pentene, (b) interpolymers of ethylene with at least one C₃-C₂₀ alpha-olefin, C₂-C₂₀ acetylenically unsaturated monomer, C₄-C₁₈ diolefin, or combinations of the 20 monomers, and (c) interpolymers of ethylene with at least one of the C₃-C₂₀ alpha-olefins, diolefins, or acetylenically unsaturated monomers in combination with other unsaturated monomers. These polymers generally have a density between about 0.850 grams per cubic centimeter and about 0.970 grams per cubic centimeter. Preferably, the density is between about 0.85 grams per cubic centimeter and about 25 0.955 grams per cubic centimeter, more preferably, between about 0.850 grams per cubic centimeter and 0.920 grams per cubic centimeter.

Ethylene/styrene interpolymers useful in the present invention include substantially random interpolymers prepared by polymerizing an olefin monomer (i.e., ethylene, propylene, or alpha-olefin monomer) with a vinylidene aromatic 30 monomer, hindered aliphatic vinylidene monomer, or cycloaliphatic vinylidene monomer. Suitable olefin monomers contain from 2 to 20, preferably from 2 to 12, more preferably from 2 to 8 carbon atoms. Preferred such monomers include ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene. Most

preferred are ethylene and a combination of ethylene with propylene or C₄₋₈ alpha-olefins. Optionally, the ethylene/styrene interpolymers polymerization components can also include ethylenically unsaturated monomers such as strained ring olefins. Examples of strained ring olefins include norbornene and C₁₋₁₀ alkyl- or C₆₋₁₀ aryl-substituted norbornenes.

Ethylene/unsaturated ester copolymers useful in the present invention can be prepared by conventional high-pressure techniques. The unsaturated esters can be alkyl acrylates, alkyl methacrylates, or vinyl carboxylates. The alkyl groups can have 1 to 8 carbon atoms and preferably have 1 to 4 carbon atoms. The carboxylate groups can have 2 to 8 carbon atoms and preferably have 2 to 5 carbon atoms. The portion of the copolymer attributed to the ester comonomer can be in the range of about 5 to about 50 percent by weight based on the weight of the copolymer, and is preferably in the range of about 15 to about 40 percent by weight. Examples of the acrylates and methacrylates are ethyl acrylate, methyl acrylate, methyl methacrylate, t-butyl acrylate, n-butyl acrylate, n-butyl methacrylate, and 2-ethylhexyl acrylate. Examples of the vinyl carboxylates are vinyl acetate, vinyl propionate, and vinyl butanoate. The melt index of the ethylene/unsaturated ester copolymers can be in the range of about 0.5 to about 50 grams per 10 minutes.

Halogenated ethylene polymers useful in the present invention include fluorinated, chlorinated, and brominated olefin polymers. The base olefin polymer can be a homopolymer or an interpolymer of olefins having from 2 to 18 carbon atoms. Preferably, the olefin polymer will be an interpolymer of ethylene with propylene or an alpha-olefin monomer having 4 to 8 carbon atoms. Preferred alpha-olefin comonomers include 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene. Preferably, the halogenated olefin polymer is a chlorinated polyethylene.

Even more preferably, when the halogenated olefin polymer is a chlorinated polyethylene, the free-radical crosslinkable polymer is present in an amount between about 20 weight percent and about 88.9 weight percent, the free-radical inducing species is present in an amount between about 0.5 weight percent and 10 weight percent, and the crosslinking-temperature profile modifier is present in amount between about 0.1 weight percent and about 5 weight percent, and the free-radical crosslinkable polymeric composition further comprises inorganic fillers in an amount

between about 10 weight percent and about 65 weight percent. This even more preferred composition is useful for flame retardant polyolefin-based compositions.

Examples of propylene polymers useful in the present invention include propylene homopolymers and copolymers of propylene with ethylene or another 5 unsaturated comonomer. Copolymers also include terpolymers, tetrapolymers, etc. Typically, the polypropylene copolymers comprise units derived from propylene in an amount of at least about 60 weight percent. Preferably, the propylene monomer is at least about 70 weight percent of the copolymer, more preferably at least about 80 weight percent.

10 Natural rubbers suitable in the present invention include high molecular weight polymers of isoprene. Preferably, the natural rubber will have a number average degree of polymerization of about 5000 and a broad molecular weight distribution.

15 Useful styrene/butadiene rubbers include random copolymers of styrene and butadiene. Typically, these rubbers are produced by free radical polymerization. Styrene/butadiene/styrene block copolymers of the present invention are a phase-separated system. The styrene/ethylene/butadiene/styrene copolymers useful in the present invention are prepared from the hydrogenation of styrene/butadiene/styrene copolymers.

20 The polybutadiene rubber useful in the present invention is preferably a homopolymer of 1,4-butadiene. Preferably, the butyl rubber of the present invention is a copolymer of isobutylene and isoprene. The isoprene is typically used in an amount between about 1.0 weight percent and about 3.0 weight percent.

25 For the present invention, polychloroprene rubbers are generally polymers of 2-chloro-1,3-butadiene. Preferably, the rubber is produced by an emulsion polymerization. Additionally, the polymerization can occur in the presence of sulfur to incorporate crosslinking in the polymer.

30 Preferably, the nitrile rubber of the present invention is a random copolymer of butadiene and acrylonitrile.

Other useful free-radical crosslinkable polymers include silicone rubbers and fluorocarbon rubbers. Silicone rubbers include rubbers with a siloxane backbone of the form $-\text{Si}-\text{O}-\text{Si}-\text{O}-$. Fluorocarbon rubbers useful in the present invention include

copolymers or terpolymers of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene with a cure site monomer to permit free-radical crosslinking.

Useful free-radical inducing species include organic peroxides, Azo free radical initiators, bicumene, oxygen, and air. Preferably, the free-radical inducing species is an organic peroxide. Preferable organic peroxides include dicumyl peroxide and Vulcup R. The organic peroxide can be added via direct injection. Oxygen-rich environments can initiate useful free-radicals. Preferably, the free-radical inducing species is present in an amount between about 0.5 weight percent and about 10 weight percent, more preferably, between about 0.5 weight percent and about 5.0 weight percent, and even more preferably, between about 0.5 weight percent and about 2.0 weight percent.

Useful examples of the crosslinking-temperature-profile modifier are free radical inhibitors such as (i) hindered amine-derived stable organic free radicals, (ii) iniferters, (iii) organometallic compounds, and (iv) aryl azooxy radical. Selection of crosslinking temperature profile modifiers is based upon determining whether the modifier will impart at least a 5-fold greater induction time over the nominal induction time.

Suitable hindered amine-derived stable organic free radicals include 2,2,6,6-tetramethyl piperidinyl oxy (TEMPO) and its derivatives. More preferably, hindered amine-derived stable organic free radicals are bis-TEMPO, oxo-TEMPO, hydroxy-TEMPO, an ester of hydroxy-TEMPO, polymer-bound TEMPO, PROXYL, DOXYL, di-tertiary butyl N oxyl, dimethyl diphenylpyrrolidine-1-oxyl, 4 phosphonoxy TEMPO, or a metal complex with TEMPO. Even more preferably, hindered amine-derived stable organic free radical is bis-TEMPO or hydroxy-TEMPO.

Iniferters are compounds capable of initiating and terminating free radical reactions. They are also capable of reversibly terminating growing polymer chains. When the crosslinking-temperature profile modifier is an iniferter, it is preferably selected from the group consisting of tetraethyl thiuram disulfide, benzyl NN diethyldithiocarbamate, dithiocarbamate, polythiocarbamate, and S benzyl dithiocarbamate.

Preferably, the crosslinking-temperature profile modifier is present in an amount between about 0.1 weight percent and about 5.0 weight percent. More preferably, it is present between 0.1 weight percent and about 2 weight percent, even

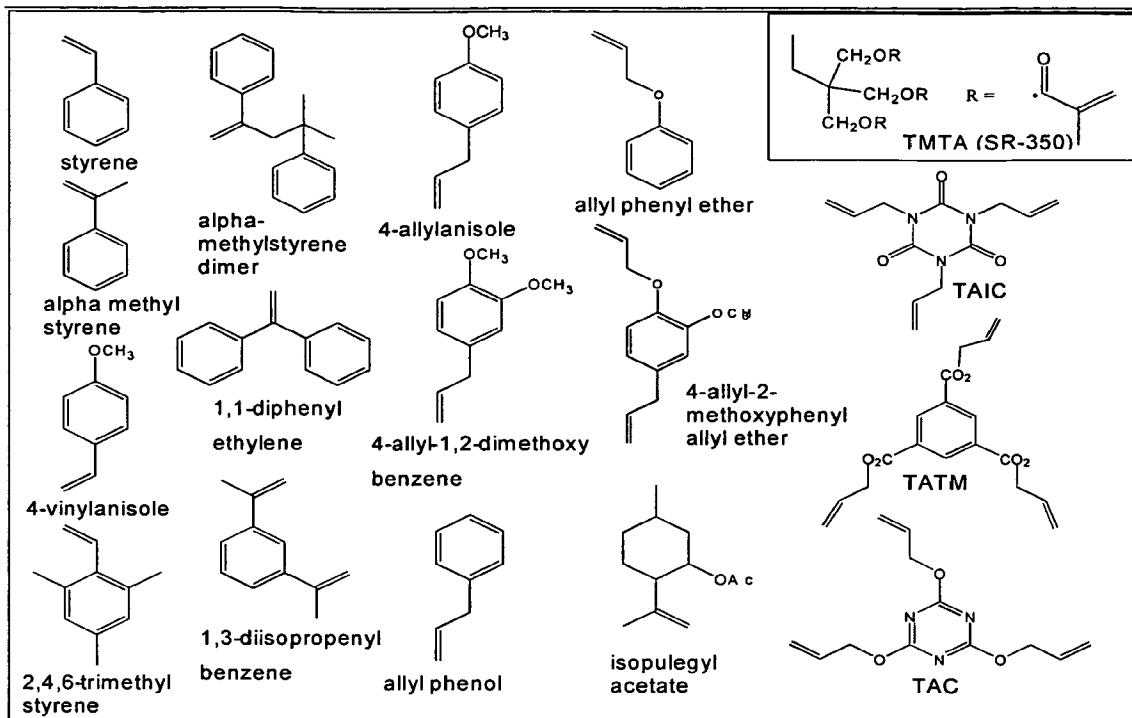
more preferably, between 0.1 weight percent and about 1 weight percent. Preferably, the free-radical inducing species and the crosslinking-temperature profile modifier are present in a ratio greater than about 1, more preferably, between about 1 to about 20.

5 The crosslinking-temperature profile modifier and free-radical inducing species can be combined with the free-radical crosslinkable polymer in a variety of ways, including direct compounding, direct soaking, and direct injection.

The crosslinkable polymeric composition can also contain an organic crosslinking modifier not having a double bond, wherein the organic crosslinking modifier and the crosslinking-temperature profile modifier synergistically (a) suppress 10 the crosslinking rate of the free-radical crosslinkable polymer at temperatures less than the nominal cure temperature of the free-radical inducing species and (b) enhance the crosslinking density at the nominal cure temperature of the free-radical inducing species. Preferably, the organic crosslinking modifier is tris(2,4-di-tert-butylphenyl)phosphite, poly[[6-[(1,1,3,3,-tetramethyl-butyl)amino]-s-triazine-2,4-diyl][2,2,6,6,-tetramethyl-4-piperidyl)imino]hexamethylene[2,2,6,6-tetramethyl-4-piperidyl)imino]], 2(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole, or blends 15 thereof.

The crosslinkable polymeric composition can also contain a nonpolar additive, 20 wherein the additive enhances the crosslinking performance without contributing to the migration of the crosslinking-temperature profile modifier to the surface of an article of manufacture prepared from the crosslinkable polymeric composition. Preferably, the nonpolar additive is decadiene or polybutadiene.

The crosslinkable polymeric composition can also contain a cure booster or a coagent to enhance the crosslinking performance of the free-radical inducing species, 25 without increasing the free-radical inducing species. Crosslinking performance enhancements can include cure rate and cure degree. The addition of a cure booster is particularly useful when the free-radical crosslinkable polymer is a chlorinated polyethylene. Useful cure boosters include polyvinyl agents and certain monovinyl agents such as alpha methyl styrene dimer, allyl pentaerythritol (or pentaerythritol triacrylate), TAC, TAIC, 4-allyl-2-methoxyphenyl allyl ether, and 1,3-di-isopropenylbenzene. Other useful cure boosters include compounds having the 30 following chemical structures.



The crosslinkable polymeric composition can also contain catalysts for increasing free-radical formation. Suitable examples of catalysts include tertiary amines, cobalt naphthenate, manganese naphthenate, vanadium pentoxide, and quaternary ammonium salt.

The crosslinkable polymeric composition can also contain a chemical or physical blowing agent, thereby rendering the crosslinkable polymeric composition expandable. Preferably, the blowing agent will be a chemical blowing agent. An example of a useful chemical blowing agent is azodicarbonamide.

Other additives are useful with the crosslinkable polymeric composition of the present invention. Those additives include scorch inhibitors, antioxidants, fillers, clays, processing aids, carbon black, flame retardants, peroxides, dispersion agents, waxes, coupling agents, mold release agents, light stabilizers, metal deactivators, plasticizers, antistatic agents, whitening agents, nucleating agents, other polymers, and colorants. The crosslinkable polymeric compositions can be highly filled.

Other suitable non-halogenated flame retardant additives include alumina trihydrate, magnesium hydroxide, red phosphorus, silica, alumina, titanium oxides, melamine, calcium hexaborate, alumina, carbon nanotubes, wollastonite, mica, silicone polymers, phosphate esters, hindered amine stabilizers, ammonium

octamolybdate, intumescence compounds, melamine octamolybdate, frits, hollow glass microspheres, talc, clay, organo-modified clay, zinc borate, antimony trioxide, and expandable graphite. Suitable halogenated flame retardant additives include decabromodiphenyl oxide, decabromodiphenyl ethane, ethylene-bis (tetrabromophthalimide), and dechlorane plus.

5 In a preferred embodiment, the present invention is an improved process for preparing a crosslinked article of manufacture. The crosslinking-temperature-profile modifier permits raising the temperature of the melt processing temperature above the nominal melt processing temperature and the temperature of the crosslinking 10 temperature portion above the nominal crosslinking temperature. Accordingly, in the invented process, the melt processing step occurs at a temperature greater than the nominal melt processing temperature and the crosslinking step occurs at a temperature greater than the nominal crosslinking temperature.

15 The combination of the free-radical crosslinkable polymer and the free-radical inducing species achieves a nominal induction time ($t_{0.04n}$) at the nominal melt processing temperature. At the nominal melt processing temperature, crosslinkable polymeric composition achieves an improved induction time ($t_{0.04i}$) of at least 5-fold greater than the nominal induction time. Preferably, the improved induction time is at least 10-fold greater than the nominal induction time. More preferably, the improved 20 induction time is at least 15-fold greater.

25 At the elevated melt processing temperature, the crosslinkable polymeric composition achieves a cure rate equal to or faster than that which is achievable in the absence of the crosslinking temperature profile modifier over the nominal crosslinking temperature profile. Also, at the elevated melt processing temperature, the crosslinkable polymeric composition maintains an induction time equal to or greater than the nominal induction time.

30 In yet another preferred embodiment, the present invention is an improved process for preparing a crosslinked article of manufacture. In the absence of the crosslinking-temperature-profile modifier, the combination of the free-radical crosslinkable polymer and the free-radical inducing species has a nominal crosslinking temperature profile and a nominal processing rate.

The crosslinking-temperature-profile modifier permits running the process at least about 20 percent faster than the nominal processing rate while the combination

achieves a cure rate equal to or faster than that which is achievable in the absence of the crosslinking temperature profile modifier. The combination also achieves an improved induction time ($t_{0.04i}$) of at least 5-fold greater than the nominal induction time at the nominal melt processing temperature. Furthermore, the combination 5 achieves an induction time equal to or greater than the nominal induction time at a melt processing temperature higher than the nominal melt processing temperature (higher-rate melt processing temperature). The higher-rate melt processing temperature is required to achieve the faster processing rate.

In this embodiment, the crosslinkable polymeric composition is melt 10 processed at the higher-rate melt processing temperature. More preferably, the crosslinking step occurs at a temperature greater than the nominal crosslinking temperature.

In another preferred embodiment, the present invention is an invented process 15 for preparing a crosslinked article of manufacture comprises the steps of (a) melt processing a crosslinkable polymeric composition, (b) forming an article of manufacture from the crosslinkable polymeric composition, and (c) crosslinking the crosslinkable polymeric composition as a formed article of manufacture. The crosslinkable polymeric composition comprises (1) a free-radical crosslinkable polymer that forms free radicals when subjected to shear energy, heat, or radiation, 20 and (2) a crosslinking-temperature-profile modifier.

In the absence of the crosslinking-temperature-profile modifier, the combination of the free-radical crosslinkable polymer, when subjected to shear energy, heat, or radiation, has a nominal crosslinking temperature profile. The nominal crosslinking temperature profile comprises a nominal melt processing 25 temperature portion, a nominal transitional temperature portion, and a nominal crosslinking temperature portion.

The crosslinking-temperature-profile modifier permits raising the temperature of the melt processing temperature portion and reducing the transitional temperature portion. Accordingly, in the invented process, the melt processing step occurs at a 30 temperature greater than nominal melt processing temperature of the combination.

The combination of the free-radical crosslinkable polymer achieves a nominal induction time at the nominal melt processing temperature. At the nominal melt processing temperature, crosslinkable polymeric composition achieves an improved

induction time of at least 5-fold greater than the nominal induction time. Preferably, the improved induction time is at least 10-fold greater than the nominal induction time. More preferably, the improved induction time is at least 15-fold greater.

5 In this preferred embodiment, the temperature of the melt processing temperature is raised by increasing the shear energy. Specifically, the preferred embodiment is particular useful in extrusion applications, wherein the screw speed is set at a higher rate to increase throughput.

10 In a yet another preferred embodiment, the present invention is a crosslinkable polymeric composition comprising a free-radical crosslinkable polymer and a crosslinking-temperature-profile modifier excluding 2,2,6,6,-tetramethyl piperidinyl oxy and derivatives thereof.

15 In a preferred embodiment, the present invention is an article of manufacture prepared by an improved process of the present invention. The benefits of the present inventions are particularly apparent with thick articles of manufacture.

20 Any number of processes can be used to prepare the articles of manufacture. Specifically useful processes include injection molding, extrusion, injection blow molding, compression molding, rotational molding, thermoforming, blowmolding, powder coating, Banbury batch mixers, fiber spinning, rotational casting, compression transferring, laminating, and calendaring. Suitable articles of manufacture include 25 wire-and-cable insulations, wire-and-cable semiconductive articles, wire-and-cable coatings and jackets, cable accessories, shoe soles, multicomponent shoe soles (including polymers of different densities and type), weather stripping, gaskets, profiles, durable goods, rigid ultradrawn tape, run flat tire inserts, construction panels, composites (e.g., wood composites), pipes, foams, and fibers (including binder fibers and elastic fibers).

EXAMPLES

The following non-limiting examples illustrate the invention.

EPDM/Modifier Masterbatch A

30 A EPDM/Modifier Masterbatch A containing a crosslinking temperature-profile modifier was prepared with Nordel™ 3722P ethylene/propylene/diene monomer pellets, zinc stearate, DFDB-5410 BK, and 4-hydroxy-TEMPO. Nordel™ 3722P ethylene/propylene/diene monomer (EPDM) had <1% diene and a Mooney

Viscosity of 20 at 125 degrees Celsius. It was commercially available from DuPont Dow Elastomers L.L.C.

The zinc stearate was commercially available from Baerlocher. The DFDB-5410 BK was a color masterbatch and commercially available from The Dow Chemical Company. The 4-hydroxy-TEMPO was commercially available from A.H. Marks.

The amounts used to prepare the EPDM/Modifier Masterbatch A are shown in Table I as weight percents.

TABLE I

Component	EPDM/Modifier Masterbatch A
Nordel™ 3722P EPDM pellets	90.00
Zinc stearate	4.00
DFDB-5410 BK	1.00
4-hydroxy-TEMPO	5.00

10

Peroxide/EPDM Masterbatch B

A peroxide-containing crosslinkable polymer was prepared as a masterbatch. The amounts used to prepare the Peroxide/EPDM Masterbatch B are shown in Table II as weight percents.

15

TABLE II

Components	Peroxide/EPDM Masterbatch B
EPDM	45.0
Treated calcined clay	35.5
Carbon black masterbatch	1.5
Zinc stearate	0.5
Polymerized 1,2-dihydro-2,2,4-trimethylquinoline	0.5
White mineral oil	12.5
Red lead	1.7
Varox™ DCP 40KE dicumyl peroxide	2.7
Sulfur, fine particles	0.1

The EPDM consisted of an EPDM or a blend of EPDMs, having \approx 5% diene content and \approx 40 Mooney viscosity at 125 degrees Celsius. The EPDM(s) were commercially available from DuPont Dow Elastomers L.L.C.

The treated calcined clay was commercially available from Engelhard. The zinc stearate was commercially available from Baerlocher. The polymerized 1,2-dihydro-2,2,4-trimethylquinoline was commercially available from R.T. Vanderbilt Company. The white mineral oil was commercially available from Citgo. The red lead was commercially available from Rhein Chemie Rubber. VaroxTM DCP 40KE dicumyl peroxide was a cure accelerator and commercially available from Geo Specialty Chemicals. The sulfur was commercially available from Rhein Chemie Rubber.

Example 1 and Comparative Example 2

A quantity of the EPDM/Modifier Masterbatch A was added to a quantity of Peroxide/EPDM Masterbatch B to prepare a free-radical crosslinkable polymer composition for use in the present invention, Example 1. Example 1 was compared to a quantity of Peroxide/EPDM Masterbatch B in the absence of the crosslinking temperature profile modifier, Comparative Example 2.

VaroxTM DCP 40KE dicumyl peroxide is a cure accelerator and commercially available from Geo Specialty Chemicals.

The amounts used to prepare Example 1 and Comparative Example 2 are shown in Table III as weight percents.

TABLE III

Component	Example 1	Comparative Example 2
Peroxide/EPDM Masterbatch B	94.89	100.00
EPDM/Modifier Masterbatch A	5.00	
Varox DCP 40KE dicumyl peroxide	0.11	

Example 1 and Comparative Example 2 were processed to make injection molded articles. Table IV shows the process condition for the melt processing temperature (Melt Temp.) and crosslinking temperature (Cure Temp.) the molded articles. All temperatures are reported in degrees Celsius. All times are reported in minutes.

The appearance of the parts is reported in the column labeled "Part." When the exemplified composition and process conditions were not conducive to making a part, the Part column identifies "NP" for cannot make parts and "Scorch" when the composition prematurely crosslinked.

5

TABLE IV

Example	Melt Temp.	Cure Temp.	Melt Time	Cure Time	Cycle Time	Part
Ex. 1	121	168	1.5	14	15.5	Good
Ex. 1	121	185	1.5	10	11.5	Good
C. Ex. 2	93	168	3	17	20.0	Good

EPDM/Modifier Masterbatch C

An EPDM/Modifier Masterbatch C containing a crosslinking temperature-profile modifier was prepared with Nordel™ 3722P ethylene/propylene/diene monomer pellets, Nipol™ D5161 nitrile rubber, 4-hydroxy-TEMPO, and dicumyl peroxide. Nordel™ 3722P ethylene/propylene/diene monomer (EPDM) had <1% diene and a Mooney Viscosity of 20 at 125 degrees Celsius. It was commercially available from DuPont Dow Elastomers L.L.C.

Nipol™ D5161 nitrile rubber was commercially available from Zeon Chemicals. The 4-hydroxy-TEMPO was commercially available from A.H. Marks. The dicumyl peroxide (DiCup R) was a cure accelerator and commercially available from Geo Specialty Chemicals.

The amounts used to prepare the EPDM/Modifier Masterbatch C are shown in Table V as weight percents.

20

TABLE V

Component	EPDM/Modifier Masterbatch C
Nordel™ 3722P EPDM pellets	44.60
Nipol™ D5161 nitrile rubber	45.00
4-hydroxy-TEMPO	6.00
dicumyl peroxide	4.40

EPDM Masterbatch D

A crosslinkable polymer was prepared as a masterbatch. The amount used to prepare the EPDM Masterbatch D are shown in Table VI as weight percents.

TABLE VI

Components	EPDM Masterbatch D
EPDM	46.0
Treated calcined clay	36.8
Carbon black masterbatch	1.5
Zinc stearate	0.5
Polymerized 1,2-dihydro-2,2,4-trimethylquinoline	0.5
White mineral oil	12.9
Red lead	1.8
Sulfur, fine particles	0.1

5

The EPDM consisted of an EPDM or a blend of EPDMs, having \approx 5% diene content and \approx 40 Mooney viscosity at 125 degrees Celsius. The EPDM(s) were commercially available from DuPont Dow Elastomers L.L.C.

10 The treated calcined clay was commercially available from Engelhard. The zinc stearate was commercially available from Baerlocher. The polymerized 1,2-dihydro-2,2,4-trimethylquinoline was commercially available from R.T. Vanderbilt Company. The white mineral oil was commercially available from Citgo. The red lead was commercially available from Rhein Chemie Rubber. The sulfur was commercially available from Rhein Chemie Rubber.

15

Example 3 and Comparative Example 4

20 A quantity of the EPDM/Modifier Masterbatch C was added to a quantity of EPDM Masterbatch D to prepare a free-radical crosslinkable polymer composition for use in the present invention, Example 3. Example 3 was compared to a quantity of EPDM Masterbatch B in the absence of the crosslinking temperature profile modifier, Comparative Example 4.

The amounts used to prepare Example 3 and Comparative Example 4 are shown in Table VIII as weight percents.

TABLE VII

Component	Example 3	Comparative Example 4
EPDM Masterbatch D	95.00	100.00
EPDM/Modifier Masterbatch C	5.00	

The crosslinking kinetics of Example 3 and Comparative Example 4 were investigated using MDR at 140 degrees Celsius (to simulate melt processing conditions where premature crosslinking is not desirable) and at 177 degrees Celsius (to simulate crosslinking conditions in which rapid and effective crosslinking is desirable). At 140 degrees Celsius, longer induction times are preferable. At 177 degrees Celsius, shorter times to the desired torque are preferable, particularly when accompanied by high crosslinking densities (or higher ultimate torque).

Figure 2 showed torque-time curves at 140 degrees Celsius while Figure 3 showed the torque-time curves at 177 degrees Celsius.

EPDM Example 5 and Comparative Example 6

An EPDM example and comparative example were prepared with Nordel™ 3722P ethylene/propylene/diene monomer pellets, a low density polyethylene, Kadox 930C zinc oxide, Translink 37 treated, calcined clay, Astor 4412 paraffin wax, Agerite MA antioxidant, dicumyl peroxide, and DFDB-5410 BK color masterbatch. The EPDM Example 5 also contained 4-hydroxy-TEMPO.

Nordel™ 3722P ethylene/propylene/diene monomer (EPDM) had <1% diene and a Mooney Viscosity of 20 at 125 degrees Celsius. It was commercially available from DuPont Dow Elastomers L.L.C. The low density polyethylene had a melt index of 2g/10 minutes and a density of 0.923 grams per cubic centimeter.

Kadox 930C zinc oxide was commercially available from Zinc Corporation of America. Translink 37 treated, calcined clay was commercially available from Engelhard. Astor 4412 paraffin wax was commercially available from Honeywell. Agerite MA antioxidant was commercially available from R. T. Vanderbilt Company. DFDB-5410 BK color masterbatch was commercially available from The Dow Chemical Company. The dicumyl peroxide (DiCup R) was an organic peroxide and commercially available from Geo Specialty Chemicals. The 4-hydroxy-TEMPO was commercially available from A. H. Marks.

The amounts used to prepare Example 5 and Comparative Example 6 are shown in Table VIII as weight percents.

TABLE VIII

Components	Example 5	Comparative Example 6
EPDM	55.81	56.05
LDPE	2.71	2.72
zinc oxide	2.71	2.72
treated, calcined clay	32.61	32.61
paraffin wax	2.71	2.72
antioxidant	0.82	0.82
peroxide	1.36	1.36
color masterbatch	1.00	1.00
4-hydroxy-TEMPO	0.27	

5 Example 5 and Comparative Example 6 were processed to make injection molded articles. Table IX shows the process condition for the melt processing temperature (Melt Temp.) and crosslinking temperature (Cure Temp.) for the molded articles. All temperatures are reported in degrees Celsius. All Cure Times are reported in seconds.

10 The appearance of the parts is reported in the column labeled "Part." When the exemplified composition and process conditions were not conducive to making a part, the Part column identifies "NP" for cannot make parts and "Scorch" when the composition prematurely crosslinked.

TABLE IX

Example	Melt Temp.	Cure Temp.	Cure Time	Gel Content (%)	Part
C. Ex. 6	120	165	140	>90%	Good
C. Ex. 6	120	165	120		NP
C. Ex. 6	135	165	200		Scorch
Ex. 5	150	165	140	>90%	Good
Ex. 5	150	180	45	>89%	Good

FR Polyolefin/Modifier Masterbatch E

5 A Flame Retardant (FR) Polyolefin/Modifier Masterbatch E containing a crosslinking temperature-profile modifier was prepared with ethylene/vinylacetate copolymer, PGA-SD White alumina trihydrate (ATH), Irganox 1010TM tetrakismethylene(3,5-di-t-butyl-4-hydroxylhydrocinnamate)methane, Vulcup R cure accelerator, and 4-hydroxy-TEMPO.

ElvaxTM 460 ethylene/vinyl acetate copolymer contained 18 percent vinyl acetate by weight and had a melt index of 2.5 grams per 10 minutes. The EVA was commercially available from DuPont.

10 PGA-SD White alumina trihydrate (ATH) was commercially available from Almatis. Irganox 1010TM tetrakismethylene(3,5-di-t-butyl-4-hydroxylhydrocinnamate)methane was a primary antioxidant and available from Ciba Specialty Chemicals Inc. Vulcup R cure accelerator was commercially available from Geo Specialty Chemicals. The 4-hydroxy-TEMPO was commercially available from 15 A.H. Marks.

The amount used to prepare the FR Polyolefin/Modifier Masterbatch E are shown in Table X as weight percents.

TABLE X

Component	FR Polyolefin/Modifier Masterbatch E
EVA	42.80
ATH	50.00
Irganox 1010 TM	0.20
Vulcup R cure accelerator	4.00
4-hydroxy-TEMPO	3.00

20 Peroxide/FR Polyolefin Masterbatch F

A peroxide-containing crosslinkable polymer was selected as the Peroxide/FR Polyolefin Masterbatch F. The selected composition was commercially available as XL 7414 peroxide-crosslinkable FR compound from Equistar.

Example 7 and Comparative Example 8

25 A quantity of the FR Polyolefin/Modifier Masterbatch E was added to a quantity of Peroxide/ FR Polyolefin Masterbatch F to prepare a free-radical

crosslinkable polymer composition for use in the present invention, Example 7. Example 7 was compared to a quantity of Peroxide/ FR Polyolefin Masterbatch F in the absence of the crosslinking temperature profile modifier, Comparative Example 8.

5 The amounts used to prepare Example 7 and Comparative Example 8 are shown in Table XI as weight percents.

TABLE XI

Component	Example 7	Comparative Example 8
Peroxide/ FR Polyolefin Masterbatch F	95.00	100.00
FR Polyolefin/Modifier Masterbatch E	5.00	

10 The crosslinking kinetics of Example 7 and Comparative Example 8 were investigated using MDR at 140 degrees Celsius (to simulate melt processing conditions where premature crosslinking is not desirable) and at 182 degrees Celsius (to simulate crosslinking conditions in which rapid and effective crosslinking is desirable). At 140 degrees Celsius, longer induction times are preferable. At 182 degrees Celsius, shorter times to the desired torque are preferable, particularly when accompanied by high crosslinking densities (or higher ultimate torque). At 182 degrees Celsius, the desired initial crosslinking torque is 16.0 pound-inches.

15 Figure 4 showed torque-time curves at 140 degrees Celsius while Figure 5 showed the torque-time curves at 182 degrees Celsius.

20 Example 7 and Comparative Example 8 were processed to make extruded articles. Table XII shows the process condition for the melt processing (both Die Temp. and Melt Temp.) of the extruded articles. All temperatures are reported in degrees Celsius. All screw speeds are reported in revolutions per minute (RPM), and all pressures are reported in pounds per square-inch (psi).

The surface quality of the parts is reported in the column labeled "Surface." A "rough" surface is indicative of premature crosslinking.

TABLE XII

Example	Die Temp.	Melt Temp.	Screw Speed	Pressure	Surface
Ex. 7	140	158	20	680	smooth
Ex. 7	140	158	30	810	smooth
Ex. 7	150	171	20	720	smooth
Ex. 7	150	170	30	880	smooth
Ex. 7	160	186	30	950	rough
C. Ex. 8	120	131	20	900	smooth
C. Ex. 8	140	162	20	860	rough
C. Ex. 8	150	174	20	1000	lump

FR Polyolefin Example 9 and Comparative Example 10

A flame retardant polyolefin example and comparative example were prepared
5 with ethylene/vinyl acetate (EVA) copolymer, PGA-SD White alumina trihydrate
(ATH), Kadox 911P heat stabilizer, distearyl-3-3-thiodipropionate (DSTDP), Irganox
1010TM tetrakis(methylene(3,5-di-t-butyl-4-hydroxy)hydrocinnamate)methane, SR 350
cure booster, Silane A-151 coupling agent, zinc stearate, and Vulcup R organic
peroxide. The flame retardant Example 9 also contained 4-hydroxy-TEMPO.

10 ElvaxTM 460 ethylene/vinyl acetate copolymer contained 18 percent vinyl
acetate by weight and had a melt index of 2.5 grams per 10 minutes. The EVA was
commercially available from DuPont.

PGA-SD White alumina trihydrate (ATH) was commercially available from
Almatis. Kadox 911P heat stabilizer was commercially available from Zinc
15 Corporation of America. Irganox 1010TM tetrakis(methylene(3,5-di-t-butyl-4-
hydroxy)hydrocinnamate)methane was a primary antioxidant and available from Ciba
Specialty Chemicals Inc. DSTDP was a secondary antioxidant and available from
Great Lakes Chemical Corporation. SR 350 cure booster was commercially available
from Sartomer Company, Inc. Silane A-151 coupling agent was commercially
20 available from GE Silicones. Zinc stearate was commercially available from
Baerlocher. Vulcup R organic peroxide was commercially available from Geo
Specialty Chemicals. The 4-hydroxy-TEMPO was commercially available from A.
H. Marks.

The amounts used to prepare Example 9 and Comparative Example 10 are shown in Table XIII as weight percents.

TABLE XIII

Components	Example 9	Comparative Example 10
EVA	43.5	44.0
ATH	48.3	48.6
heat stabilizer	2.2	2.2
primary antioxidant	0.7	0.7
secondary antioxidant	1.5	1.5
cure booster	0.8	0.8
coupling agent	0.6	0.6
zinc stearate	0.4	0.4
organic peroxide	1.7	1.2
4-hydroxy-TEMPO	0.3	

5 The crosslinking kinetics of Example 9 and Comparative Example 10 were investigated using MDR at 140 degrees Celsius (to simulate melt processing conditions where premature crosslinking is not desirable) and at 182 degrees Celsius (to simulate crosslinking conditions in which rapid and effective crosslinking is desirable). At 140 degrees Celsius, longer induction times are preferable. At 182
10 degrees Celsius, shorter times to the desired torque are preferable, particularly when accompanied by high crosslinking densities (or higher ultimate torque).

Figure 6 showed torque-time curves at 140 degrees Celsius while Figure 7 showed the torque-time curves at 182 degrees Celsius.

CPE Example 11 and Comparative Example 12

15 A peroxide-crosslinkable chlorinated polyethylene example and comparative example were prepared with TYRINTM CM0836 chlorinated polyethylene. The compositions also contained CSX-618 carbon black, SR350 cure booster, and Dicup R organic peroxide. The peroxide-crosslinkable composition exemplifying the present invention further contained 4-hydroxy-TEMPO.

The TYRINT™ CM0836 chlorinated polyethylene contained 36% chlorine and had a Mooney Viscosity of 94 at 121 degrees Celsius. It was commercially available DuPont Dow Elastomers, L.L.C.

5 The carbon black was commercially available from Cabot Corporation. The SR520 cure booster was commercially available from Sartomer Company, Inc. The dicumyl peroxide (DiCup R) was an organic peroxide and commercially available from Geo Specialty Chemicals. The 4-hydroxy-TEMPO was commercially available from A. H. Marks.

10 The amounts used to prepare Example 11 and Comparative Example 12 are shown in Table XIV as weight percents.

TABLE XIV

Component	Example 11	Comparative Example 12
CPE	73.4	74.0
Carbon black	23.0	23.0
SR520	1.5	1.5
DiCup R	2.0	1.5
4-hydroxy-TEMPO	0.1	

15 The crosslinking kinetics of Example 11 and Comparative Example 12 were investigated using MDR at 120 degrees Celsius and 140 degrees Celsius (to simulate melt processing conditions where premature crosslinking is not desirable) and at 182 degrees Celsius (to simulate crosslinking conditions in which rapid and effective crosslinking is desirable). At 120 and 140 degrees Celsius, longer induction times are preferable. At 182 degrees Celsius, shorter times to the desired torque are preferable, particularly when accompanied by high crosslinking densities (or higher ultimate 20 torque). At 205 degrees Celsius, the desired initial crosslinking torque is 40.0 pound-inches.

Figure 8 showed torque-time curves at 120 degrees Celsius while Figure 9 showed the torque-time curves at 140 degrees Celsius. Figure 10 showed the torque-time curves at 182 degrees Celsius.

25 Example 11 and Comparative Example 12 were processed to make extruded articles. Table XV shows the process condition for the melt processing (both Die

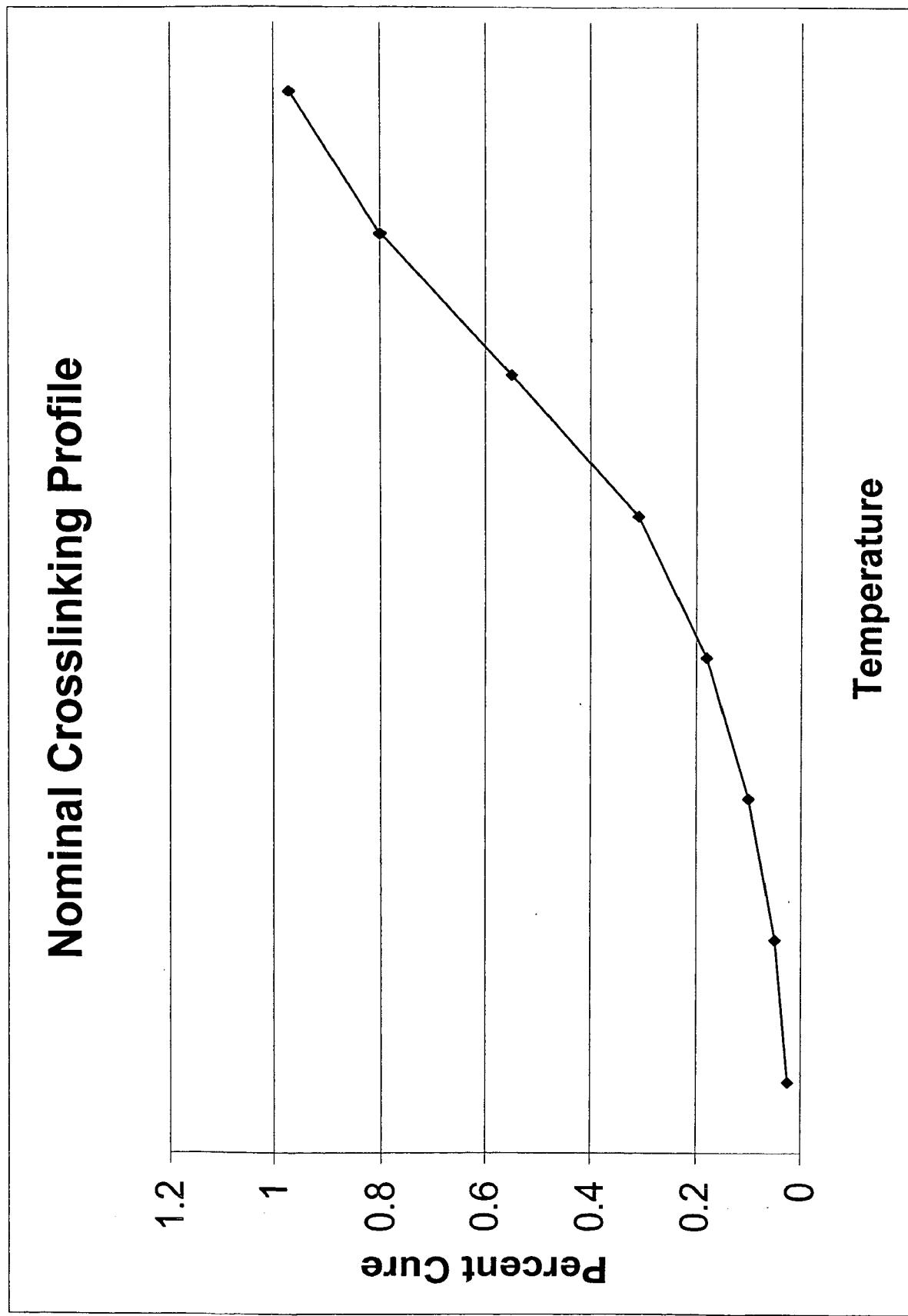
Temp. and Melt Temp.) of the extruded articles. All temperatures are reported in degrees Celsius. All screw speeds are reported in revolutions per minute (RPM), and all pressures are reported in pounds per square-inch (psi).

5 The surface quality of the parts is reported in the column labeled "Surface." A "rough" surface is indicative of premature crosslinking.

TABLE XV

Example	Die Temp.	Melt Temp.	Screw Speed	Pressure	Surface
Ex. 11	120	120	15	4500	Smooth
Ex. 11	120	125	30	5900	Smooth
Ex. 11	130	130	15	4600	Smooth
Ex. 11	130	136	30	5700	Smooth
Ex. 11	140	140	15	4800	Rough
Ex. 11	140	147	30	6100	Rough
C. Ex. 12	110	110	15	5500	Rough
C. Ex. 12	120	120	15	4800	Lump

FIG. 1



FT6.2

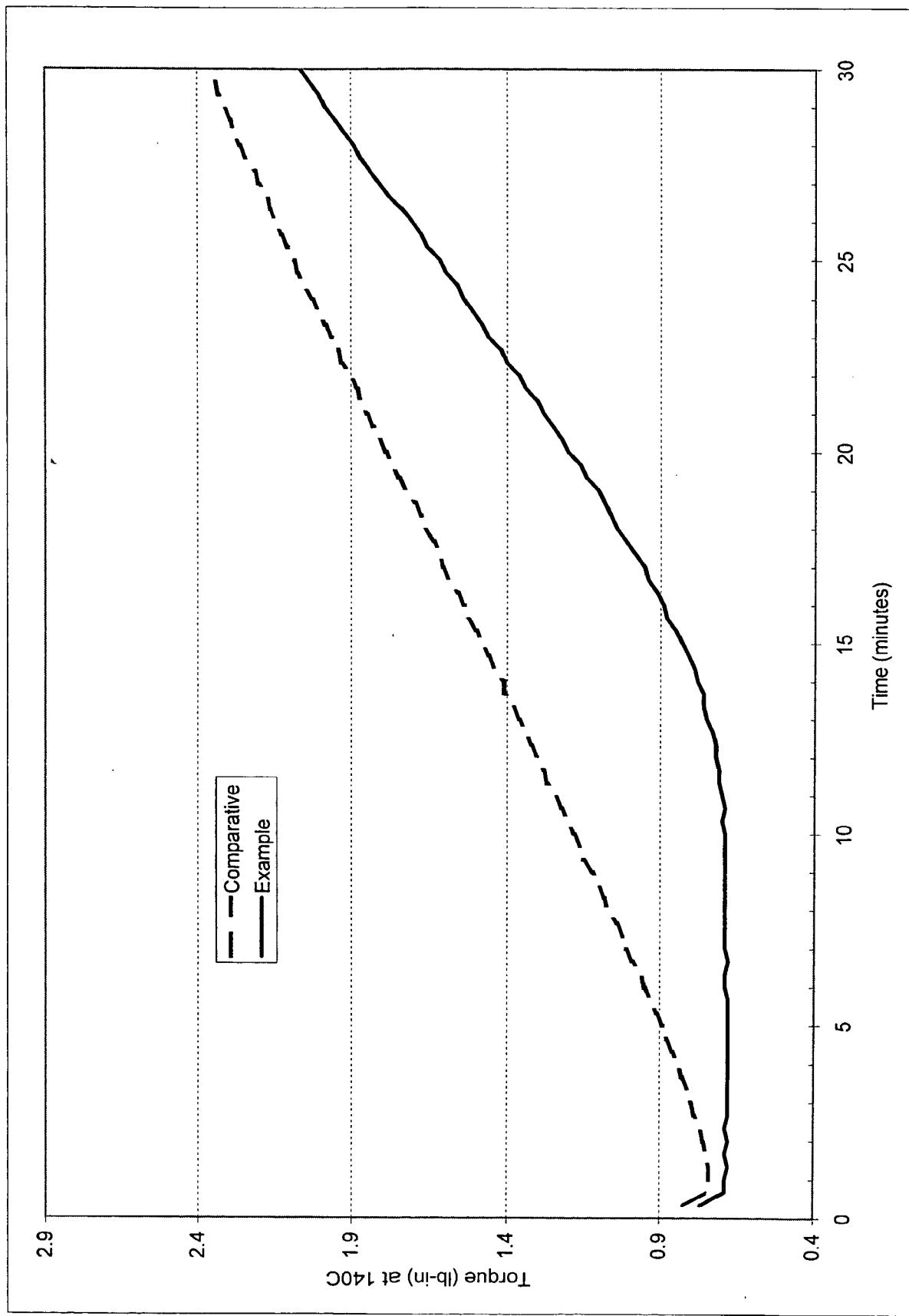


FIG. 3

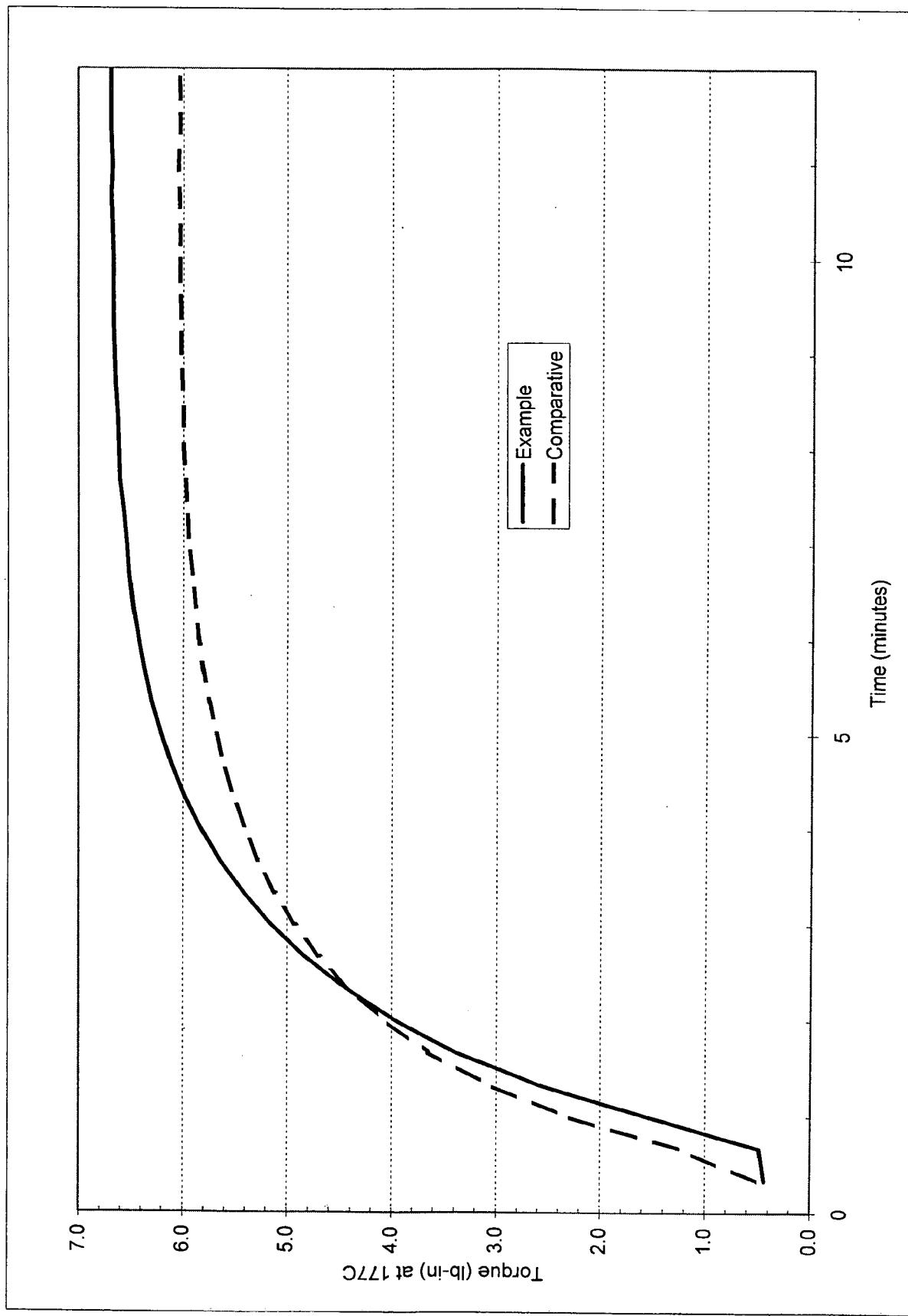


FIG. 4

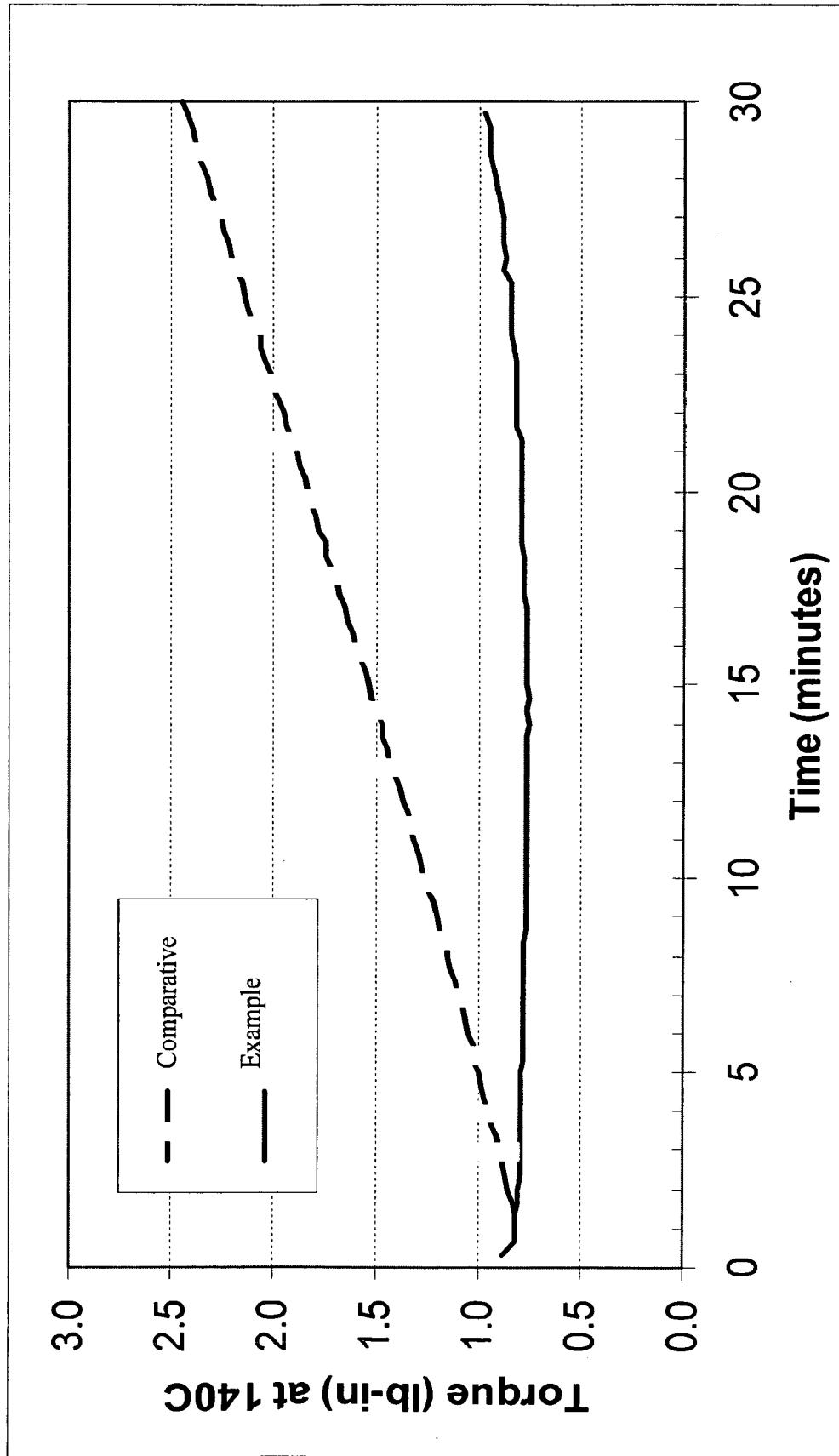


FIG. 5

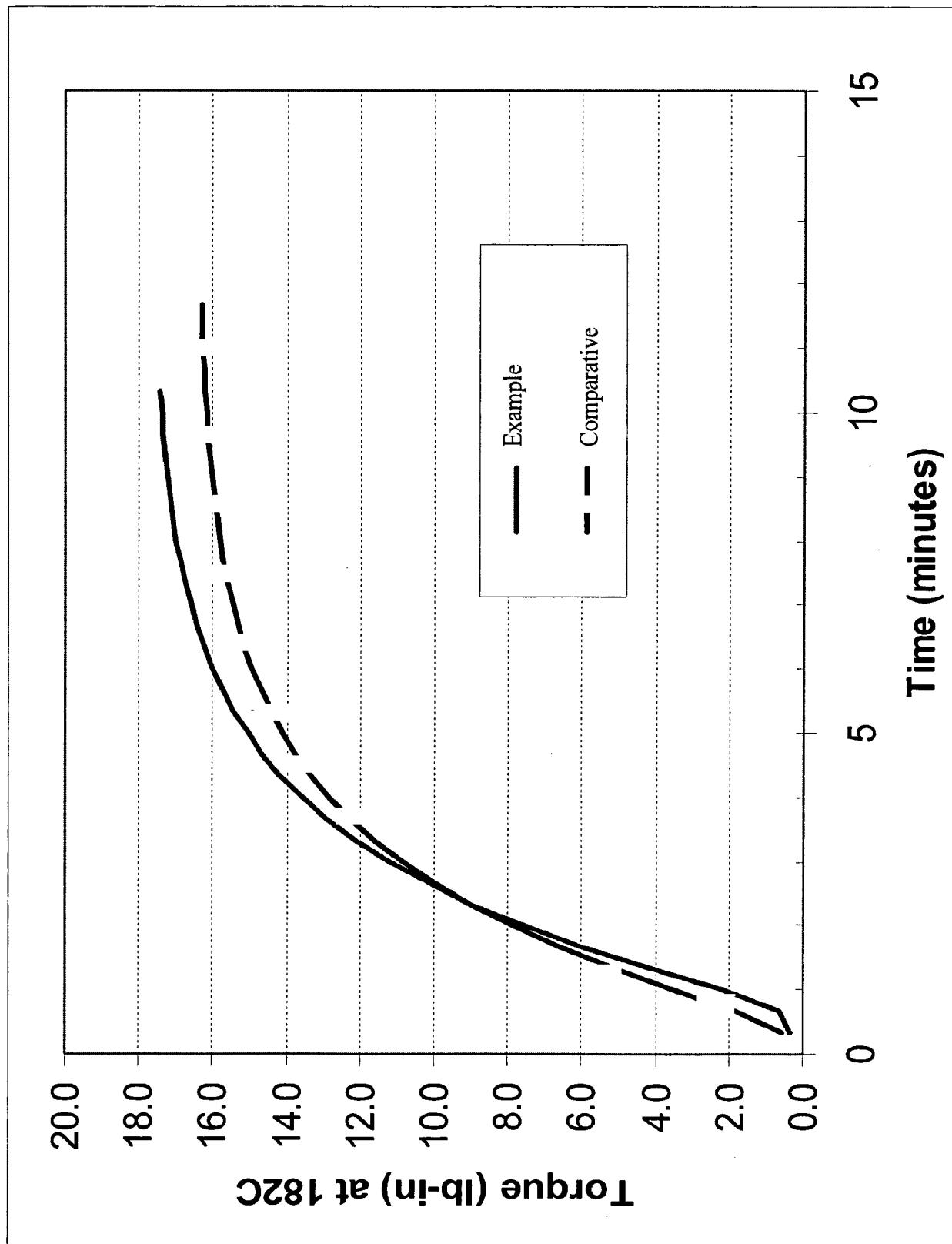


FIG. 4

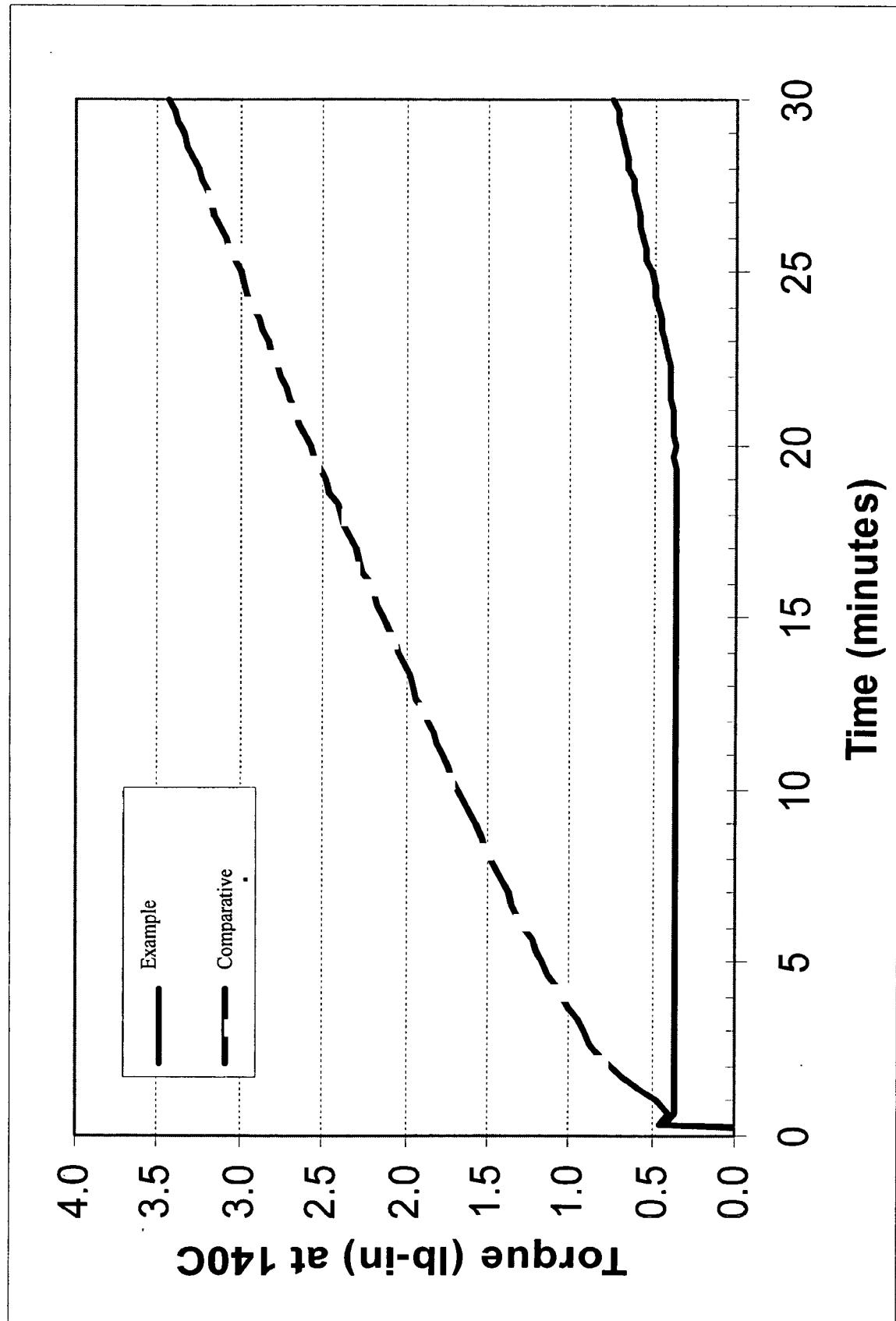


FIG. 7

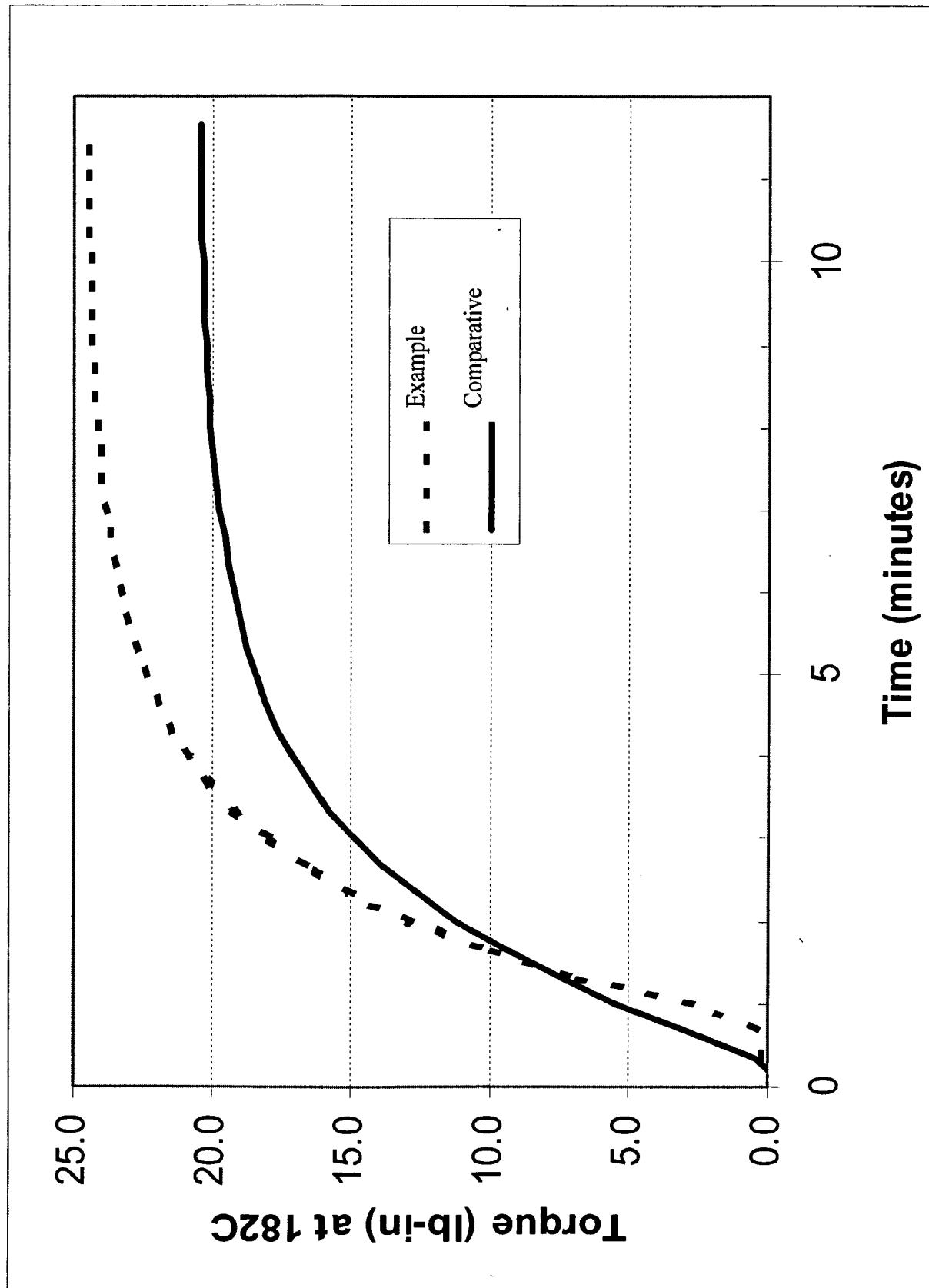


Figure 8: Crosslinking Kinetics at 120°C

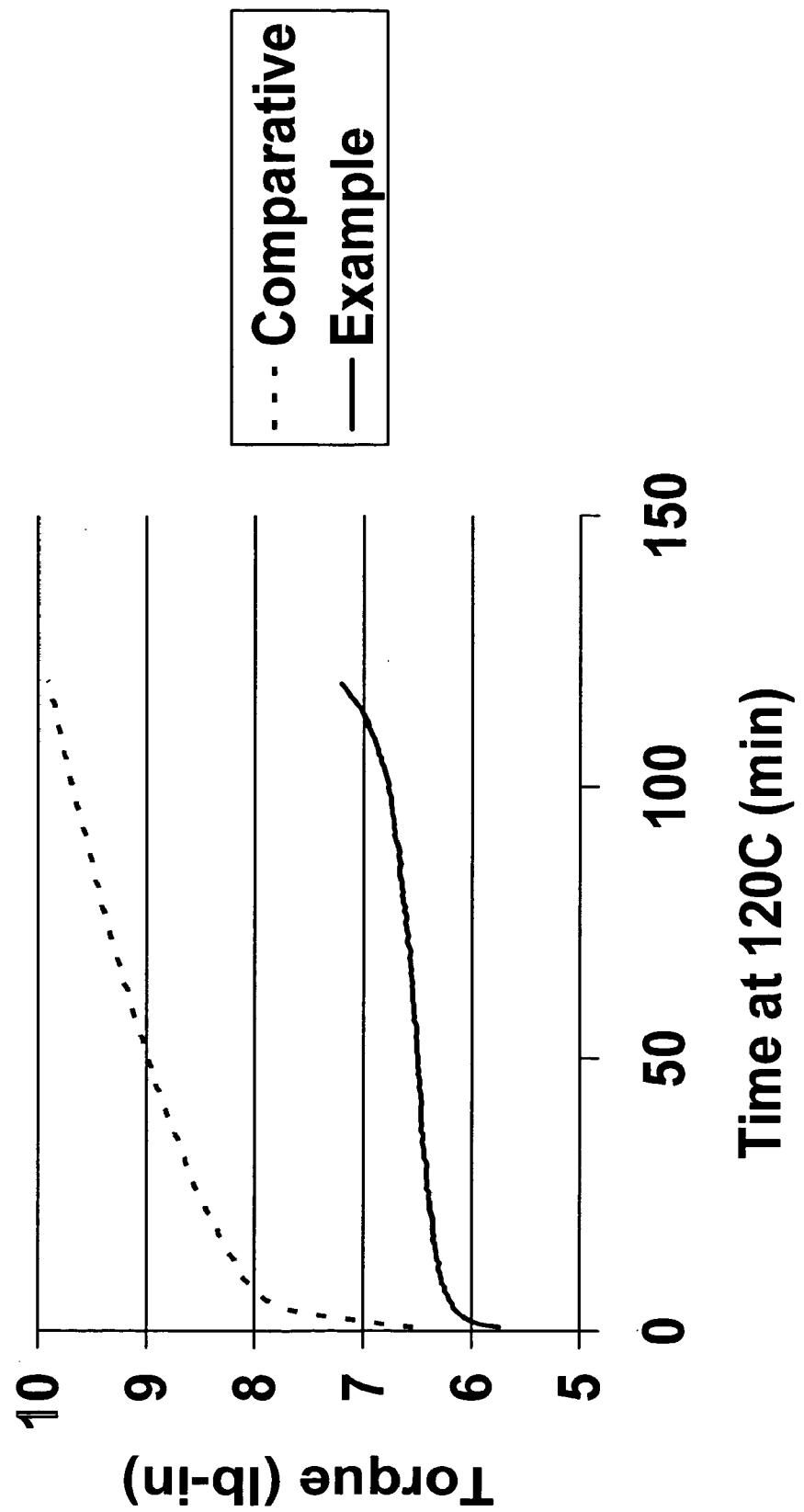


Figure 9: Crosslinking Kinetics at 140C

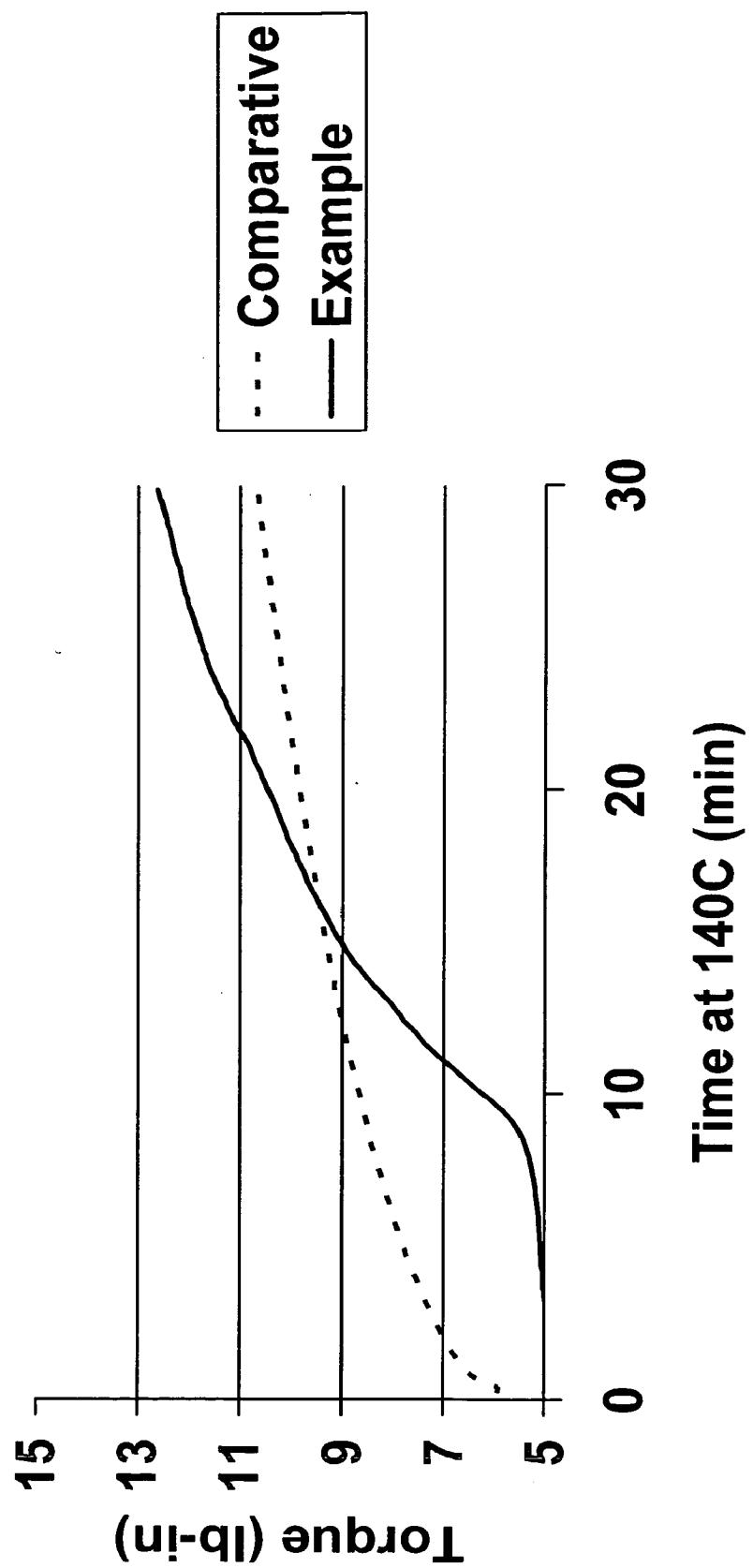


Figure 10: Crosslinking Kinetics at 182C

